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<b>(21) International Application Number:</b> PCT/EP98/03005 <b>(22) International Filing Date:</b> 14 May 1998 (14.05.98) <b>(30) Priority Data:</b> 9711849.1      6 June 1997 (06.06.97)      GB <b>(71) Applicant (for all designated States except AU BB CA CY GB GH IE KE LK LS MN MW NZ SD SG SZ TT UG):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). <b>(71) Applicant (for AU BB CA CY GB GH IE KE LK LS MN MW NZ SD SG SZ TT UG only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).	<b>(72) Inventors:</b> BLOKZIJL, Wilfried; Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). ENGBERTS, Jan; Universiteit Groningen, Broerstraat 5, NL-9712 CP Groningen (NL). KEVELAM, Jan; Universiteit Groningen, Broerstraat 5, NL-9712 CP Groningen (NL). KHOSHDEL, Ezat; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). KOEK, Jean, Hypolites; Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). VAN DE PAS, Johannes, Comelis; Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). VERSLUIS, Pieter; Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). VISSER, Adrianus; Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> POLYMERIC MATERIALS  <b>(57) Abstract</b>  An oligomer or polymer of the formula (I): $Q^1 - X^1 - Y^1 - Z - W$ wherein $Q^1$ represents a hydrophobic moiety, $-X^1$ and $-Y^1$ are independently each absent or represent a suitable linking group, $-Z$ represents a hydrophilic chain; and $-W$ represents hydrogen or a group of the formula $-Y^2 - X^2 - Q^2$ , each of $-X^2$ , $-Y^2$ and $-Q^2$ being independently selected from the values for $X^1$ , $Y^1$ and $Q^1$ as hereinbefore defined.		

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POLYMERIC MATERIALSFIELD OF THE INVENTION

5 The present invention is concerned with polymeric materials which are useful for endowing desirable rheological properties to a particular class of aqueous liquid detergent compositions. This class of aqueous compositions comprises those which contain sufficient detergent-active  
10 material and, optionally, sufficiently dissolved electrolyte to result in a structure of lamellar droplets dispersed in a continuous aqueous phase.

BACKGROUND OF THE INVENTION

15

Lamellar droplets are a particular class of surfactant structures which, inter alia, are already known from a variety of references, e.g. H.A. Barnes, 'Detergents', Ch.2 in K.Walters (Ed), 'Rheometry: Industrial Applications', J.  
20 Wiley & Sons, Letchworth 1980.

Such lamellar dispersions are used to endow properties such as consumer-preferred flow behaviour and/or turbid appearance. Many are also capable of suspending  
25 particulate solids such as detergency builders or abrasive particles. Examples of such structured liquids without suspended solids are given in US patent 4 244 840, whilst examples where solid particles are suspended are disclosed in specifications EP-A-160 342: EP-A-38 101: EP-A-104 452  
30 and also in the aforementioned US 4 244 840. Others are disclosed in European Patent Specification EP-A-151 884, where the lamellar droplets are called 'spherulites'.

The presence of lamellar droplets in a liquid detergent product may be detected by means known to those skilled in the art, for example optical techniques, various  
5 rheometrical measurements, X-ray or neutron diffraction, and electron microscopy.

The droplets consist of an onion-like configuration of concentric bi-layers of surfactant molecules, between which  
10 is trapped water or electrolyte solution (aqueous phase). Systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties.

15 The viscosity and stability of the product depend on the volume fraction of the liquid which is occupied by the droplets. Generally speaking, the higher the volume fraction of the dispersed lamellar phase (droplets), the better the stability. However, higher volume fractions  
20 also lead to increased viscosity which in the limit can result in an unpourable product. This results in compromise being reached. When the volume fraction is around 0.6 or higher, the droplets are just touching (space-filling). This allows reasonable stability with an  
25 acceptable viscosity (say no more than 2.5 Pas, preferably no more than 1 Pas at a shear rate of  $21\text{s}^{-1}$ ). This volume fraction also endows useful solid-suspending properties.

A complicating factor in the relationship between stability  
30 and viscosity on the one hand and, on the other, the volume fraction of the lamellar droplets, is the degree of flocculation of the droplets. When flocculation occurs

between the lamellar droplets at a given volume fraction, the viscosity of the corresponding product will increase owing to the formation of a network throughout the liquid.

Flocculation may also lead to instability because deformation of the lamellar droplets, owing to flocculation, will make their packing more efficient. Consequently, more lamellar droplets will be required for stabilisation by the space-filling mechanism, which will again lead to a further increase of the viscosity.

10

The volume fraction of droplets is increased by increasing the surfactant concentration whereas flocculation between the lamellar droplets occurs when a certain threshold value of the electrolyte concentration is crossed at a given level of surfactant (and fixed ratio between any different surfactant components). Thus, in practice, the effects referred to above mean that there is a limit to the amounts of surfactant and electrolyte which can be incorporated whilst still having acceptable product properties. In principle, higher surfactant levels are required for increased detergency (cleaning performance). Increased electrolyte levels can also be used for better detergency, or are sometimes sought for secondary benefits such as building.

25

According to the specification of EP-A-346 995, the dependency of stability and/or viscosity upon volume fraction is favourably influenced by incorporating into the lamellar dispersion, a deflocculating polymer comprising a hydrophilic backbone and one or more hydrophobic side-chains.

30

The theory of function of these deflocculating polymers is that the hydrophobic chains are anchored in the outer bilayer of the lamellar droplet. The hydrophilic part is extended outwards. These hydrophilic 'brushes' are responsible for the steric stabilisation of the droplets, provided that the 'brushes' exceed a certain length. For surfactant blends in common use, the optimum length of the polymer hydrophobic chain, in order to be anchored into the bilayer is in the order of  $C_{12} - C_{15}$ , about the length of the surfactants in the droplet. However, for reducing viscosity, the number of hydrophobic anchors per polymer molecule should be limited to one, otherwise one polymer chain could link two droplets which results in gelling of the dispersion due to bridging.

15

EP-A-438 215 discloses preparation of acrylic acid telomers with a functional terminal group, using a secondary alcohol chain transfer agent which may, for example be a  $C_6 - C_{12}$  monofunctional secondary alcohol. These materials are described as detergent additives, in particular sequestrants or anti-precipitants. The materials are produced using polymerisation initiators such as ditertiary butyl peroxide. In the description of various different possible initiators, there is mentioned lauryl peroxide. However, there is no example described of use of lauryl peroxide to produce a  $C_{12}$  hydrophobe - terminated polyacrylate. Moreover, the telomers are not disclosed as having any efficacy in controlling the rheological properties of lamellar droplet-structured aqueous detergent liquids and indeed, aqueous detergent liquids are not mentioned at all.

Some specific kinds of deflocculating polymers which contain only one hydrophobic moiety and which is attached to an end position of a hydrophilic chain, are disclosed in EP-A-623 670.

5

Various sub-types are described for the deflocculating polymers in EP-A-623 670. However, many of those actually exemplified are thiol polyacrylates, that is to say, materials formed by polymerisation of acrylic acid in the  
10 presence of a hydrophobic chain transfer agent having from five to twenty five carbon atoms and a terminal-SH group, in a radical polymerisation process. Analagous materials having a thia linkage between the hydrophilic and hydrophobic parts of the molecule are disclosed in US-A-5  
15 489 395, US-A-5 489 397 and EP-A-691 399.

It is also now believed that the molecular weight of the deflocculating polymer should exceed a certain value in order to avoid 'building in' of the whole polymer inside  
20 the droplets. The applicants have discovered that the optimum molecular weight seems to be about 2500, a compromise of deflocculating efficiency and cost efficiency.

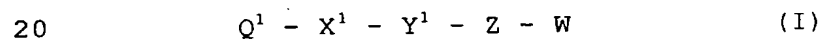
25 Typical examples of the polymer disclosed in EP-A-346 995 are made by a radical copolymerization of acrylic acid and laurylmethacrylate. This results in a random distribution of lauryl chains over the polymer. As a consequence, most of the polymer molecules have one hydrophobic chain per  
30 molecule. However, a reasonable fraction of the polymer molecules have more than one hydrophobic anchors per

molecule. The last fraction may give rise to a viscosity increase due to bridging.

The polymers as disclosed in EP-A-623 679, EP-A-691 399 and 5 US-A-5 489 397 being 'end-capped', in principle have a lower fraction of polymer molecules with more than one hydrophobic anchor as compared with the polymers described in EP-A-346 995. However, the described synthesis routes of these end-capped polymers are rather limited and produce 10 polymers which are not optimal in their performance. A new class of polymers constituted by the first aspect of the present invention overcomes, according to the particular new polymer in question, one or more of these drawbacks.

## 15 SUMMARY OF THE INVENTION

Thus, the present invention now provides an oligomer or polymer of formula (I)



wherein  $Q^1$ - represents a hydrophobic moiety,  $-X^1-$  and  $-Y^1-$  are independently each absent or represent a suitable linking group,  $-Z-$  represents a hydrophilic chain; and 25  $-W$  represents hydrogen or a group of formula  $-Y^2-X^2-Q^2$ , each of  $-X^2$ ,  $-Y^2$  and  $-Q^2$  being independently selected from the values for  $X^1$ ,  $Y^1$  and  $Q^1$  as hereinbefore defined.

## DETAILED DESCRIPTION OF THE INVENTION

30

### Oligomer or Polymer



Preferably  $Q^1$  represents an optionally substituted  $C_5 - C_{30}$  alkyl,  $C_5 - C_{30}$  alkenyl or  $C_5 - C_{30}$  aralkyl group, or a hydrophobic monomer residue, such as from lauryl methacrylate or a hydrophobically modified TEMPO (2,2,6,6-tetramethylpiperdiny-1-oxy) moiety. Alkyl, alkenyl or aralkyl groups most preferably have from 8 to 18 carbon atoms and are preferably straight-chained or have only limited branching. Preferably,  $X^1$  is absent or represents a group of formula  $(-CH_2-)_n$  where  $n$  is 1 or 2 or  $X^1$  is phenyl. Preferably,  $Y^1$  is absent or represents a carbonyl group, an ester linkage, a hydroxy  $C_{1-5}$  alkyl group or a silyl group of formula  $(-SiR^1R^2)$ , where  $R^1$  and  $R^2$  independently represent  $-CH_3$  or  $-C_2H_5$ ; or else  $Y^1$  is a thia-, aza-, carboxy- (i.e. ester), carboxy-aza-, phosphoryl-, phosphonyl- or phosphinyl- linkage, but then with the proviso that  $W$  is not hydrogen.

The group  $-Z-$  is preferably a linear, branched or slightly crosslinked molecular composition containing one or more types of relatively hydrophilic monomer units. Preferably the hydrophilic monomers themselves are sufficiently water soluble to form at least a 1% by weight solution when dissolved in water. The only limitations to the structure of  $-Z-$  are that the resultant polymer of formula (I) must be suitable for incorporation in an active-structured aqueous liquid detergent composition and that a polymer corresponding to the hydrophilic moiety alone, i.e.  $H-Z-H$  is relatively soluble in water, in that the solubility in water at ambient temperature and at a pH of 3.0 to 12.5 is preferably more than 1 g/l, more preferred more than 5 g/l, most preferred more than 10 g/l.

Preferably the group -Z- is predominantly linear; more preferably the main chain of the backbone constitutes at least 50% by weight, preferably more than 75%, most preferred more than 90% by weight of the backbone.

5

The group -Z- is generally composed of monomer units, which can be selected from a variety of units available for the preparation of polymers.

10 Examples of types of monomer units for inclusion alone or in combination in -Z- are:

(i) Unsaturated C<sub>1</sub>-C<sub>6</sub> acids, ethers, alcohols, aldehydes, ketones or esters. Preferably these monomer units are mono-unsaturated. Examples of suitable monomers are

15 acrylic acid, methacrylic acid, maleic acid, crotonic acid, itaconic acid, aconitic acid, citraconic acid, vinyl-methyl ether, vinyl sulphonate, vinylalcohol obtained by the hydrolysis of vinyl acetate, acrolein, alkenyl alcohol and vinyl acetic acid. The corresponding salts, e.g. alkali  
20 metal salts such as the sodium salt, are also included.

(ii) Cyclic units, either being unsaturated or comprising other groups capable of forming inter-monomer linkages. In linking these monomers the ring-structure of the monomers  
25 may either be kept intact, or the ring structure may be disrupted to form the backbone structure. Examples of cyclic monomer units are sugar units, for instance saccharides and glucosides; alkoxy units such as ethylene oxide and hydroxy propylene oxide; and maleic anhydride.

30

(iii) Other units, for example glycerol, polyalkylene oxide(s) or unsaturated polyalcohol(s) .

Each of the above mentioned monomer units for inclusion in -Z- may be substituted with groups such as amino, ammonium, amide, sulphonate, sulphate, phosphonate, phosphate, 5 hydroxy, carboxyl and oxide groups.

The group -Z- is preferably composed of one or two monomer types but also possible is the use of three or more different monomer types in one hydrophilic backbone.

10 Examples of preferred hydrophilic backbones are:

homopolymers of acrylic acid, copolymers of acrylic acid and maleic acid, poly (2-hydroxy ethyl acrylate), polysaccharides, cellulose ethers, polyglycerols, polyacrylamides, polyvinylalcohol/polyvinylether

15 copolymers, poly sodium vinyl sulphonate, poly 2-sulphato ethyl methacrylate, polyacrylamido methyl propane sulphonate and copolymers of acrylic acid and trimethylol propane triacrylate.

20 Optionally, the group -Z- may also contain small amounts of relatively hydrophobic units, e.g. those derived from polymers having a solubility of less than 1g/l in water, provided that the overall solubility of the hydrophilic polymer backbone still satisfies the solubility

25 requirements as specified hereabove. Examples of relatively water insoluble polymers are polyvinyl acetate, polymethyl methacrylate, polyethyl acrylate, polyethylene, polypropylene, polystyrene, polybutylene oxide, polypropylene oxide and polyhydroxy propyl acetate.

30

Preferred sub-classes of the oligomers or polymers of formula (I) (hereinafter referred to as "materials of the

invention"), include respectively, those where W is hydrogen, those where W is  $-Y^2-X^2-Q^2$ , some or all of  $X^2$ ,  $Y^2$  and  $Q^2$  respectively differing from  $X^1$ ,  $Y^1$  and  $Q^1$  and those where W is  $-Y^2-X^2-Q^2$ ,  $X^2$ ,  $Y^2$  and  $Q^2$  each being the same as  $X^1$ ,  $Y^1$  and  $Q^1$ .

If W is hydrogen, there is only a single hydrophobic moiety attached to one end of the hydrophilic moiety. Such materials are ideally suited as deflocculating materials.

10 If W is a group  $-Y^2-X^2-Q^2$  then there is a respective hydrophobic group at either end of the hydrophobic moiety.

Such materials may be employed for deliberate bridging of lamellar droplets, e.g. to increase viscosity.

15 Of course, as mentioned above, often deflocculation is needed to inhibit viscosity increase at high volume fractions so that in principle, bridging can be undesirable. However, the bridging materials having a pair of hydrophobic groups (W not hydrogen) are within the ambit  
20 of the present invention. For example, a predetermined blend of materials of the invention may be used, comprising one deflocculating material to control stability and one bridging material to increase viscosity in a controlled fashion.

25

The bridging material has, on average, more than one hydrophobic ( $Q^1/Q^2$ ) groups per molecule and preferably two or more such hydrophobic groups. As a consequence the molecular weight ( $M_w$ ) of the bridging material is larger  
30 than  $(x.M_i + M_o)$ , preferably larger than  $(x.M_i + 2M_o)$  and more preferably larger than  $2(x.M_i + M_o)$ , with x being the molecular ratio between hydrophilic monomers and

hydrophobic monomers,  $M_i$  being the average molecular weight of the hydrophilic groups and  $M_o$  the average molecular weight of the hydrophobic groups.

5 The bridging polymer is preferably prepared using conventional aqueous polymerisation procedures, but employing a process wherein the polymerisation is carried out in the presence of a suitable cosolvent and wherein the ratio of water to cosolvent is carefully monitored so as to  
10 keep the polymer as it forms in a sufficiently mobile condition and to prevent unwanted homopolymerisation and precipitation of the polymer from the hydrophobic monomer.

The process of the invention provides a product which is stable and clear and which exhibits no gelling or product  
15 separation on standing. Suitable cosolvents are selected from the group consisting of isopropanol, n-propanol, acetone, lower ( $C_1$  to  $C_4$ ) alcohols, esters and ketones and wherein the water to cosolvent ratio is smaller than 1.5, more preferably less than 1.0, more preferably less than  
20 0.75, and especially less than 0.5.

The use of a better defined mixture of a deflocculating material and of a bridging material allows a degree of control of rheology not possible with the "cocktail" of  
25 polymers resulting from the process of EP-A-346 995.

Nevertheless, it should be appreciated that any method of forming either the deflocculating ( $W=H$ ) or bridging ( $W = Y^2-X^2-Q^2$ ) oligomers or polymers of formula (I) will not form  
30 100% pure materials. However, sample oligomers or polymers according to the present invention will have a high weight percentage of oligomer or polymer species having a

structure of formula (I), although not necessarily all of that percentage will have the same structure of formula (I). Thus, a preferred sample or batch of oligomer and/or polymer material the present invention may have at least 5 50% by weight of its total of oligomers and/or polymers having the general formula (I) as defined in claim 1, or optionally, of any preferred sub-class of polymers or oligomers of formula (I) as defined in the description or any other claim. This weight percentage is more 10 preferably, in ascending order of preference, at least 65%, 70%, 75%, 80%, 85% or 90% by weight of the total batch or sample.

Materials of the present invention preferably have a 15 molecular weight of at least 500, more preferably at least 1000, still more preferably at least 2000. Also, their molecular weight is preferably no more than 50,000, more preferably no more than 30,000 and especially, no more than 10,000, less than 5,000.

20

Any reference herein to determination of oligomer or polymer molecular weight refers to the number-averaged degree of polymerisation as determined using  $^1\text{H-NMR}$  spectroscopy by comparing the intensities of the NMR peaks 25 corresponding to the terminal methyl group (from the initiator) at ca. 0.95 ppm and the polymer backbone  $-\text{CH}_2-$  and  $-\text{CH}-$  at 2.2 ppm, respectively. This so-called determination of end groups is a well-known procedure, cf. J.C. Bevington, J.R. Ebdon, and T.N. Huckerby, in *NMR Spectroscopy of Polymers*, R.N. Ibbett (Ed.), Chapman & 30 Hall, Glasgow: 1993, and R.G. Garmon in *Polymer Molecular*

*Weights, Part I*, P.E. Slade, Jr. (Ed.), Marcel Dekker, New York: 1975.

The aforementioned method demands high accuracy of the  
5 integration of the NMR spectra, which is especially important if the degree of polymerisation exceeds ca. 100.

To check its accuracy a high-molecular weight poly(acrylic acid) was synthesised using 1 mol% of AIBN, in the absence of transfer agent. The molecular weight of this polymer  
10 was determined using both the end group (NMR) method and viscosimetry. The intrinsic viscosity of the polymer was determined to be  $0.193 \pm 0.008$  dl/g. From this value, the viscosity-averaged molecular weight ( $M_v$ ) was calculated to be 51500 (cf. S. Newman, W.R. Krigbaum, C. Laugier, and  
15 P.J. Flory, *J. Polym. Sci* 1954, 14 451). From NMR, the number-averaged molecular weight ( $M_n$ ) was found to be ca. 25000. It is known from the literature H.F. Mark, N.H. Biktales, C.G. Overberger, G. Menger and J.I. Kroschwitz (Eds), 'Encyclopedia of Polymer Science and Engineering',  
20 p. 280; 2nd ed. Vol. 3; Wiley, New York 1985 that for polydisperse samples  $M_n < M_v < M_w$ . Since  $M_w/M_n$  could be as high as 5-10 for unfractionated poly(acrylic acid) samples at high conversion, the determined ratio of  $M_v/M_n = 2$  is therefore reliable.

25

#### Preparation of the Oligomer or Polymer

Preferred methods of preparing materials of the invention will vary according to the kind of material required.

30 Thus, a second aspect of the present invention provides a method of preparing an oligomer or polymer of formula (I)

as hereinbefore defined, by reacting a compound of formula (IV)



5

wherein  $Q^1$ ,  $X^1$  and  $Y^1$  are as hereinbefore defined and  $Y^2$  is a reactive hydrogen or a free radical, with a precursor material, in the presence of an initiator.

10 The term "reactive hydrogen" is herein defined as referring to a bond heat of formation between 96 and 80 kcal/mol, preferably between 92 and 85 kcal/mol (as mentioned in 'Handbook of Chemistry and Physics', pages F223-F229, 56 ed. 1975-1976) (such as a TEMPO derivative). The  
15 precursor material is a monomer or prepolymer, containing at least one polymerizable group, said monomer or polymer being capable of forming a group of formula -Z-W as hereinbefore defined.

20 The compound of formula (IV) may for example be a compound wherein  $X^1$  is absent,  $Y^1$  represents a carbonyl group or -COH( $R^5$ )- wherein  $R^5$  is a  $C_{1-4}$  alkyl group; and if W is not hydrogen, then  $Y^1$  can be a thia group.

25 Alternatively, an oligomer or polymer of formula (I) may be prepared by reacting a compound of formula (V)



30 wherein  $Q^1$  is as hereinbefore defined with a precursor material as hereinbefore defined and  $Q^1-G-Q^1$  is a molecule capable of cleavage to form a radical of formula  $-Q^1-X^1-Y^1$ .



In the compound of formula (V), G may for example be -CO-O-  
O-CO- or -N=N- and the precursor material may comprise a  
radical-forming compound and one or more monomers for  
5 forming the group -Z-.

A radical initiator containing the hydrophobic group  $Q^1$  is  
a compound which can initiate chemical reactions by  
producing free radicals as mentioned in Kirk-Othmer,  
10 "Encyclopaedia of Chemical Technology, 4th edition, volume  
14, page 431-460. A suitable example of such a radical  
initiator is dilauroyl peroxide ( $Q$  = undecyl). Other  
examples: diisononanoyl peroxide ( $Q$  = iso-octyl),  
dicumylperoxide ( $Q$  = 1-cyano-cyclohex-1-yl).

15

Control of both hydrophobic endgroups ( $Q^1$ ,  $Q^2$ ) can also be  
achieved by, for example, a so-called living  
polymerisation. A possible procedure involves a controlled  
radical polymerisation, involving TEMPO (2,2,6,6-  
20 tetramethylpiperidiny-1-oxy) and a normal, e.g. peroxide  
radical initiator, as described in J.Am.Chem.Soc. 1994,  
116, 11185-11186, by Craig J. Hawker.

Typically in a first step one starts with a compound of  
25 formula (IV), TEMPO and initiator. The product obtained  
from this reaction is then used in a second step by heating  
it in the presence of a precursor as hereinbefore defined  
giving a polymer with a hydrophilic backbone having on the  
one end a hydrophobic group and on the other the  
30 thermolabile TEMPO group. Heating this polymer in the  
presence of a hydrophobic monomer (e.g. laurylmethacrylate)

inserts the monomer resulting in a copolymer with two hydrophobic endgroups.

In another embodiment one could use a hydrophobically  
5 modified TEMPO molecule obviating the last insertion step.

In still another embodiment one starts with a mix of TEMPO, initiator and a hydrophobic monomer giving a hydrophobic starting block which can be further elaborated as above.

10

In yet another embodiment, one could use a compound of formula (V) as initiator in combination with TEMPO as described above, for giving a copolymer with two hydrophobic endgroups.

15

#### Detergent Compositions

A further aspect of the present invention provides an aqueous liquid detergent composition in the form of a  
20 dispersion of lamellar droplets, the composition comprising water, surfactant, a material of the invention and optionally electrolyte. Such compositions are hereinafter referred to as compositions according to the present invention. Materials of the invention can be incorporated  
25 in such aqueous detergent lamellar dispersions to provide stable, pourable products preferably wherein the volume fraction of the lamellar phase is 0.5-0.6 or higher.

#### Lamellar Droplet Phase

30

The volume fraction of the lamellar droplet phase may be determined by the following method. The composition is

centrifuged, say at 40,000 G for 12 hours, to separate the composition into a clear (continuous aqueous) layer, a turbid active-rich (lamellar) layer and (if solids are suspended) a solid particle layer. The conductivities of the continuous aqueous phase, the lamellar phase and of the total composition before centrifugation are measured. From these, the volume fraction of the lamellar phase is calculated, using the Bruggeman equation, as disclosed in American Physics, 24, 636 (1935). When applying the equation, the conductivity of the total composition must be corrected for the conductivity inhibition owing to any suspended solids present. The degree of correction necessary can be determined by measuring the conductivity of a model system. This has the formulation of the total composition but without any surfactant. The difference in conductivity of the model system, when continuously stirred (to disperse the solids) and at rest (so the solids settle), indicates the effect of suspended solids in the real composition. Alternatively, the real composition may be subjected to mild centrifugation (say 2,000 G for 1 hour) to just remove the solids. The conductivity of the upper layer is that of the suspending base (aqueous continuous phase with dispersed lamellar phase, minus solids).

25

It should be noted that, if the centrifugation at 40,000 G fails to yield a separate continuous phase, the conductivity of the aforementioned model system at rest can serve as the conductivity of the continuous aqueous phase. For the conductivity of the lamellar phase, a value of 0.8 mS.cm<sup>-1</sup> can be used, which is typical for most systems. In

30

any event, the contribution of this term in the equation is often negligible.

Preferably, the viscosity of the aqueous continuous phase is less than 25 mPas, most preferably less than 15 mPas, especially less than 10 mPas, these viscosities being measured using a capillary viscometer, for example an Ostwald viscometer.

Sometimes, it is preferred for the compositions of the present invention to have solid-suspending properties (i.e. capable of suspending solid particles). Therefore, in many preferred examples, suspended solids are present. However, sometimes it may also be preferred that the compositions of the present invention do not have solid suspending properties, this is also illustrated in the examples.

In practical terms, i.e. as determining product properties, the term 'deflocculating' in respect of the polymer means that the equivalent composition, minus the polymer, has a significantly higher viscosity and/or becomes unstable. Although within the ambit of the present invention, relatively high levels of the deflocculating polymers can be used in those systems where a viscosity reduction is brought about; typically levels as low as from about 0.01% by weight to about 1.0% by weight can be capable of reducing the viscosity at  $21\text{ s}^{-1}$  by up to 2 orders of magnitude.

Especially preferred embodiments of the present invention exhibit less phase separation on storage and have a lower

viscosity than an equivalent composition without any of the deflocculating polymer.

It is conventional in patent specifications relating to aqueous structured liquid detergents to define the stability of the composition in terms of the volume separation observed during storage for a predetermined period at a fixed temperature. In fact, this can be an over-simplistic definition of what is observed in practice. Thus, it is appropriate here to give a more detailed description.

For lamellar droplet dispersions, where the volume fraction of the lamellar phase is below 0.6 and the droplets are flocculated, instability is inevitable and is observed as a gross phase separation occurring in a relatively short time. When the volume fraction is below 0.6 but the droplets are not flocculated, the composition may be stable or unstable. When it is unstable, a phase separation occurs at a slower rate than in the flocculated case and the degree of phase separation is less.

When the volume fraction of the lamellar phase is below 0.6, whether the droplets are flocculated or not, it is possible to define stability in the conventional manner. In the context of the present invention, stability for these systems can be defined in terms of the maximum separation compatible with most manufacturing and retail requirements. That is, the 'stable' compositions will yield no more than 2% by volume phase separation as evidenced by appearance of 2 or more separate layers when stored at 25°C for 21 days from the time of preparation.

In the case of the compositions where the lamellar phase volume fraction is 0.6 or greater, it is not always easy to apply this definition. In the case of the present invention, such systems may be stable or unstable, 5 according to whether or not the droplets are flocculated. For those that are unstable, i.e. flocculated, the degree of phase separation may be relatively small, e.g. as for the unstable non-flocculated systems with the lower volume fraction. However, in this case the phase separation will 10 often not manifest itself by the appearance of a distinct layer of continuous phase but will appear distributed as 'cracks' throughout the product. The onset of these cracks appearing and the volume of the material they contain are almost impossible to measure to a very high degree of 15 accuracy. However, those skilled in the art will be able to ascertain instability because the presence of a distributed separate phase greater than 2% by volume of the total composition will readily be visually identifiable by such persons. Thus, in formal terms, the above-mentioned 20 definition of 'stable' is also applicable in these situations, but disregarding the requirement for the phase separation to appear as separate layers.

Especially preferred embodiments of compositions according 25 to the present invention yield less than 0.1% by volume visible phase separation after storage at 25°C for 90 days from the time of preparation.

It must also be realised that there can be some difficulty 30 in determining the viscosity of an unstable liquid.

When the volume fraction of the lamellar phase is less than 0.6 and the system is deflocculated or when the volume fraction is 0.6 or greater and the system is flocculated, then phase separation occurs relatively slowly and  
5 meaningful viscosity measurement can usually be determined quite readily. For all compositions of the present invention it is usually preferred that their viscosity is not greater than 2.5 Pas, most preferably no more than 1.0 Pas, and especially not greater than 750 mPas at a shear  
10 rate of  $21\text{s}^{-1}$ .

When the volume fraction of the lamellar phase is less than 0.6 and the droplets are flocculated, then often the rapid phase separation occurring makes a precise determination of  
15 viscosity rather difficult. However, it is usually possible to obtain a figure which, whilst appropriate, is still sufficient to indicate the effect of the deflocculating polymer in the compositions according to the present invention.

20

Generally, the amount of material of oligomer and/or polymer of the present invention in any aqueous detergent lamellar dispersion will be from 0.01% to 5.0% by weight in the composition, most preferably from 0.1% to 2.0%.

25

Although it is possible to form lamellar dispersions of surfactant in water alone, in many cases it is preferred for the aqueous continuous phase to contain dissolved electrolyte. As used herein, the term electrolyte means  
30 any ionic water-soluble material. However, in lamellar dispersions, not all the electrolyte is necessarily dissolved but may be suspended as particles of solid

because the total electrolyte concentration of the liquid is higher than the solubility limit of the electrolyte. Mixtures of electrolytes also may be used, with one or more of the electrolytes being in the dissolved aqueous phase and one or more being substantially only in the suspended solid phase. Two or more electrolytes may also be distributed approximately proportionally, between these two phases. In part, this may depend on processing, e.g. the order of addition of components. On the other hand, the terms 'salts' includes all organic and inorganic materials which may be included, other than surfactants and water, whether or not they are ionic, and this term encompasses the sub-set of the electrolytes (water-soluble materials).

The only restriction on the total amount of detergent-active material and electrolyte (if any) is that in the compositions of the invention, together they must result in formation of an aqueous lamellar dispersion. Thus, within the ambit of the present invention, a very wide variation in surfactant types and levels is possible. The selection of surfactant types and their proportions, in order to obtain a stable liquid with the required structure will be fully within the capability of those skilled in the art.

#### 25 Detergent Active Material

However, it can be mentioned that an important sub-class of useful compositions is those where the detergent-active material comprises blends of different surfactant types. Typical blends useful for fabric washing compositions include those where the primary surfactant(s) comprise



nonionic and/or non-alkoxylated anionic and/or alkoxylated anionic surfactant.

In many (but not all) cases, the total detergent-active material may be present at from 2% to 60% by weight of the total composition, for example from 5% to 40% and typically from 10% to 30% by weight. However, one preferred class of compositions comprises at least 15%, most preferably at least 25% and especially at least 30% of detergent-active material based on the weight of the total composition. In the case of blends of surfactants, the precise proportions of each component which will result in such stability and viscosity will depend on the type(s) and amount(s) of the electrolytes, as is the case with conventional structured liquids.

In the widest definition the detergent-active material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol. 1, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch", H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C<sub>6</sub>-C<sub>18</sub>) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C<sub>8</sub>-C<sub>18</sub>) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulphonates, particularly sodium linear secondary alkyl (C<sub>10</sub>-C<sub>15</sub>) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C<sub>6</sub>-C<sub>18</sub>) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty

acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by  
5 reacting alpha-olefins ( $C_8$ - $C_{20}$ ) with sodium bisulphite and those derived from reacting paraffins with  $SO_2$  and  $Cl_2$  and then hydrolyzing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins,  
10 particularly  $C_{10}$ - $C_{20}$  alpha-olefins, with  $SO_3$  and then neutralising and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium ( $C_{11}$ - $C_{15}$ ) alkyl benzene sulphonates and sodium ( $C_{16}$ - $C_{18}$ ) alkyl sulphates.

15

Also possible is that part or all of the detergent active material is a stabilising surfactant, which has an average alkyl chain length greater than 6 C-atoms, and which has a salting out resistance, greater than, or equal to 6.4.

20 These stabilising surfactants are disclosed in EP-A-328 177. Examples of these materials are alkyl polyalkoxylated phosphates, alkyl polyalkoxylated sulphosuccinates; dialkyl diphenyloxide disulphonates; alkyl polysaccharides and mixtures thereof.

25

It is also possible, and sometimes preferred, to include an alkali metal soap of a long chain mono- or dicarboxylic acid for example one having from 12 to 18 carbon atoms. Typical acids of this kind are oleic acid, ricinoleic acid  
30 and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palm kernel oil or mixtures

thereof. The sodium or potassium soaps of these acids can be used.

#### Water

5

Preferably the amount of water in the composition is from 5 to 95%, more preferred from 25 to 75%, most preferred from 30 to 50%. Especially preferred less than 45% by weight.

#### 10 Electrolyte

The compositions optionally also contain electrolyte in an amount sufficient to bring about structuring of the detergent-active material. Preferably though, the  
15 compositions contain from 1% to 60%, especially from 10 to 45% of a salting-out electrolyte. Salting-out electrolyte has the meaning ascribed to in specification EP-A-79 646. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included, provided if of  
20 a kind and in an amount compatible with the other components and the composition is still in accordance with the definition of the invention claimed herein. Some or all of the electrolyte (whether salting-in or salting-out), or any substantially water-insoluble salt which may be  
25 present, may have detergency builder properties. In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. The builder material is any capable of reducing the level of free calcium ions  
30 in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil

removed from the fabric and the dispersion of the fabric softening clay material.

#### Detergency Builder

5

Examples of phosphorous-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of  
10 inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used.

Examples of non-phosphorous-containing inorganic detergency  
15 builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and  
20 zeolites.

In the context of inorganic builders, we prefer to include electrolytes which promote the solubility of other electrolytes, for example use of potassium salts to promote  
25 the solubility of sodium salts. Thereby, the amount of dissolved electrolyte can be increased considerably (crystal dissolution) as described in UK patent specification GB 1 302 543.

30 Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates,

polyacetyl carboxylates, carboxymethyloxysuccinates, carboxymethyloxymalonates, ethylene diamine-N,N-disuccinic acid salts, polyepoxysuccinates, oxydiacetates, triethylene tetramine hexa-acetic acid salts, N-alkyl imino diacetates  
5 or dipropionates, alpha sulpho- fatty acid salts, dipicolinic acid salts, oxidised polysaccharides, polyhydroxysulphonates and mixtures thereof.

Specific examples include sodium, potassium, lithium,  
10 ammonium and substituted ammonium salts of ethylenediamino-tetraacetic acid, nitrilo-triacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid, tartrate mono succinate and tartrate di succinate.

15 In the context of organic builders, it is also desirable to incorporate polymers which are only partly dissolved in the aqueous continuous phase. This allows a viscosity reduction (owing to the polymer which is dissolved whilst incorporating a sufficiently high amount to achieve a  
20 secondary benefit, especially building, because the part which is not dissolved does not bring about the instability that would occur if substantially all were dissolved).

#### Other Polymers

25

Examples of partly dissolved polymers include many of the polymer and co-polymer salts already known as detergency builders. For example, may be used (including building and non-building polymers) polyethylene glycols, polyacrylates,  
30 polymaleates, polysugars, polysugarsulphonates and co-polymers of any of these. Preferably, the partly dissolved polymer comprises a co-polymer which includes an alkali

metal salt of a polyacrylic, polymethacrylic or maleic acid or anhydride. Preferably, compositions with these copolymers have a pH of above 8.0. In general, the amount of viscosity-reducing polymer can vary widely according to the formulation of the rest of the composition. However, typical amounts are from 0.5 to 4.5% by weight.

It is further possible to include in the compositions of the present invention, alternatively, or in addition to the partly dissolved polymer, yet another polymer which is substantially totally soluble in the aqueous phase and has an electrolyte resistance of more than 5 grams sodium nitrilotriacetate in 100 ml of a 5% by weight aqueous solution of the polymer, said second polymer also having a vapour pressure in 20% aqueous solution, equal or less than the vapour pressure of a reference 2% by weight or greater aqueous solution of polyethylene glycol having an average molecular weight of 6,000; said second polymer having a molecular weight of at least 1,000.

20

The incorporation of the soluble polymer permits formulation with improved stability at the same viscosity (relative to the composition without the soluble polymer) or lower viscosity with the same stability. The soluble polymer can also reduce viscosity drift, even when it also brings about a viscosity reduction. Here, improved stability and lower viscosity mean over and above any such effects brought about by the deflocculating polymer.

30 It is especially preferred to incorporate the soluble polymer with a partly dissolved polymer which has a large insoluble component. That is because although the building

capacity of the partly dissolved polymer will be good (since relatively high quantities can be stably incorporated), the viscosity reduction will not be optimum (since little will be dissolved). Thus, the soluble  
5 polymer can usefully function to reduce the viscosity further, to an ideal level.

The soluble polymer can, for example, be incorporated at from 0.05 to 20% by weight, although usually from 0.1 to  
10 10% by weight of the total composition is sufficient, and especially from 0.2 to 3.5 - 4.5% by weight. It has been found that the presence of deflocculating polymer increase the tolerance for higher levels of soluble polymer without stability problems. A large number of different polymers  
15 may be used as such a soluble polymer, provided the electrolyte resistance and vapour pressure requirements are met. The former is measured as the amount of sodium nitrolotriacetate (NaNTA) solution necessary to reach the cloud point of 100 ml of a 5% w/w solution of the polymer  
20 in water at 25°C, with the system adjusted to neutral pH, i.e. about 7. This is preferably effected using sodium hydroxide. Most preferably, the electrolyte resistance is 10 g NaNTA, especially 15g. The latter indicates a vapour pressure low enough to have sufficient water binding  
25 capability, as generally explained in the applicants' specification GB-A-2 053 249. Preferably, the measurement is effected with a reference solution at 10% by weight aqueous concentration, especially 18%.

30 Typical classes of polymers which may be used as the soluble polymer, provided they meet the above requirements,



include polyethylene glycols, Dextran, Dextran sulphonates, polyacrylates and polyacrylate/maleic acid co-polymers.

The soluble polymer must have an average molecular weight of at least 1,000 but a minimum average molecular weight of 2,000 is preferred.

The use of partly soluble and the use of soluble polymers as referred to above in detergent compositions is described in our European patent specifications EP-A-301 882 and EP-A-301 883.

#### Hydrotrope

Although it is possible to incorporate minor amounts of hydrotropes such as lower alcohols (e.g. ethanol) or alkanolamines (e.g. triethanolamine), in order to ensure integrity of the lamellar dispersion we prefer that the compositions of the present invention are substantially free from hydrotropes. By hydrotrope is meant any water soluble agent which tends to enhance the solubility of surfactants in aqueous solution.

#### Other Optional Ingredients

25

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather booster such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, fabric softeners such as clays, amines and amine oxides; lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium

percarbonate; peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, 5 perfumes, enzymes such as proteases, amylases, lipases (including Lipolase (Trade Mark) ex Novo) and cellulases, germicides and colourants, oily-soil release polymers, such as Poly Ethylene Terephthalate - Poly Oxy Ethylene Terephthalates or (partly) sulphonate versions thereof 10 (including Permalose and Aquaperle (Trademarks) ex. ICI, Gerol and Repe-O-Tex (Trademarks) ex. Rhone-Poulenc and Sokalan HP22 (Trademark) ex. BASF); anti-redeposition agents, such as sodium carboxy methyl cellulose; anti-dye transfer agents, such as PVP, PVI and co-polymers thereof.

15

Amongst these optional ingredients, as mentioned previously, are agents to which lamellar dispersions without deflocculating polymer are highly stability-sensitive and by virtue of the present invention, can be 20 incorporated in higher, more useful amounts. These agents cause a problem in the absence of deflocculating polymer because they tend to promote flocculation of the lamellar droplets. Examples of such agents are soluble polymers, soluble builders such as succinate builders, fluorescers 25 like Blankophor RKH, Tinopal LMS, and Tinopal DMS-X and Blankophor BBH as well as metal chelating agents, especially of the phosphonate type, for example the Dequest range sold by Monsanto.

EXAMPLES

The invention will now be illustrated by way of the following Examples, in all Examples, unless stated to the contrary, all percentages are by weight.

**Example 1:        Synthesis of mono-endcapped hydrophobically-modified poly(sodium acrylate) using a hydrophobic initiator in dioxane: solution polymerisation**

10

**Materials:**

monomer     : acrylic acid (AA), 5g (69.4 mmol), freshly-distilled (Janssen, 99%)

15

initiator   : dilauroylperoxide (DLP), 0.57 g (1.43 mmol) (Aldrich)

solvent     : dioxane, 50 ml (Merck, pro analysi)

**Synthesis:**

A 250 ml round-bottomed flask was loaded with 5 g of acrylic acid, 50 ml of dioxane and 0.57g of dilauroylperoxide. The flask was connected to a reflux condenser fitted with a  $\text{CaCl}_2$ -tube and was heated on an oil bath at 80°C with stirring. The reaction mixture was kept at this temperature overnight. After cooling to room temperature, the clear, slightly viscous solution was precipitated in 300 ml of pentane to remove most of the dioxane. The viscous precipitate was dissolved in dry methanol. The methanolic solution was slowly precipitated in a stirred solution of 3.6 g (66.7 mmol) of sodium methoxide in 100 ml of dry methanol. The white solid was filtered off under reduced pressure. The crude product was dried in vacuo at 30°C to remove most of the remaining

dioxane and methanol. The polymer was dissolved in water to obtain a solution of about 5-10% (w/w). The polymer was completely neutralised by adding sodium hydroxide until the pH was 9, and the solution was freeze-dried. In order to  
5 remove the last traces of solvent, the polymer was finely powdered and dried at 60°C over P<sub>2</sub>O<sub>5</sub> in vacuo for at least 2 hours.

Characterisation:

- 10 The absence of monomer was established by <sup>1</sup>H-NMR using the characteristic peaks for the acrylic hydrogens at ca. 6 ppm. We note the importance of pH in recording the NMR spectra. At pH 1 the peaks are broader and shifted upfield relative to a solution of pH 10. This is due to a  
15 conformational change of the polymer from a compact globule at low pH to a more extended coil at high pH (cf. J. Jager, Ph. D. Thesis, Groningen, 1987). All NMR spectral data presented correspond to pH 10.
- 20 MALDI-TOFSPEC was employed to unambiguously demonstrate that the polymer molecules mainly contain only one hydrophobic chain.

The characteristics of the polymer were as follows:

- 25 - Degree of polymerisation (DP) = 97; MW = 9200 (see addendum 1)  
- Efficiency of initiation = 25%

The product is essentially an undecyl or a dodecyl chain connected to (on average) 97 sodium acrylate moieties, i.e.

- 30 in structural terms according to formula I:  $Q^1 = C_{11}H_{23}-$ ;  $Y^1 = -COO-$  or absent;  $X^1$  is absent;  $Z = (CH_2-C(H)(COONa))_{97}-$ ;  $W=H$ .

Example 2:        Synthesis of mono-endcapped hydrophobically-  
modified poly(sodium acrylate) using a hydrophobic  
initiator in 2-butanone (MEK): precipitation  
5 polymerisation.

Materials:

monomer        : acrylic acid (AA), 5 g (69.4 mmol), freshly-  
                 distilled  
10 initiator    : dilauroylperoxide<sup>4</sup> (DLP), 1.14 g (2.86 mmol)  
solvent        : 2-butanone (MEK), 50 ml (Merck, pro analysi)

The synthesis, purification and characterisation of the  
polymer were analogous to those employed in Example 1 with  
15 the following exceptions.

During the reaction in MEK, a glassy precipitate was formed  
which is the desired polymer. The polymerisation was  
complete after 5 hours. After reaction, the mixture was  
20 cooled to room temperature, the solvent was decanted and  
the solid was dissolved in methanol. In principle, the MEK  
could be re-used. The methanolic solution containing the  
poly(acrylic acid) was precipitated in pentane, and worked-  
up as described above.

25

The characteristics of the polymer were as follows:

- DP = 123; MW = 11700 (see addendum 2)
- Efficiency of initiation = 10%

The structure of the polymer according to formula I reads:

30  $Q^1 = C_{11}H_{23}-$ ;  $Y^1 = -COO-$  or absent;  $X^1$  is absent;  $Z = -(CH_2-$   
 $C(CH)(COONa))_{123}-$ ; W is H.

Example 3: Synthesis of mono-endcapped hydrophobically-modified poly(sodium acrylate) using 2-tetradecanol as a hydrophobic transfer agent in 2-butanone (MEK): precipitation polymerisation.

5

Materials:

monomer : acrylic acid (AA), 5 g (69.4 mmol), freshly-distilled

10 initiator : azo-bis-isobutyronitril (AIBN), 0.14 g (0.85 mmol)

transfer agent : 2-tetradecanol, 7.49 g (34.9 mmol)

solvent : 2-butanone (MEK), 50 ml, pro analysi

Synthesis:

15 The same procedure was followed as described for Example 2. However, instead of n-dodecyl-mercaptane, 2-tetradecanol was used. This alcohol was synthesised from 1-bromododecane and distilled acetaldehyde according to a literature procedure (Pickard, R.H.; Kenyon, J. *Ind Eng.*  
20 *Chem.* 1940, 32, 206).

Characterisation:

In order to prove that the hydrophobic modification was not due to esterification of the alcohol with the acrylic acid,  
25 the polymer was treated with aqueous sodium hydroxide (pH 12) for 1 week. This treatment did not affect the NMR spectral characteristics of the polymer during this time, which provides evidence that no hydrolysis had taken place. Therefore, the alcohol is probably connected to the  
30 poly(acrylate) moiety through a C-O bond, which is most likely due to incorporation of the secondary alcohol by a radical transfer mechanism.

The characteristics of the polymer were as follows:

- DP = 112; MW = 10600

The chemical structure of the polymer reads, according to  
5 formula I:

$Q^1 = C_{12}H_{25}-$ ;  $Y^1 = -C(CH_3)(OH)-$ ;  $X^1 = \text{absent}$ ;  $Z = -(CH_2-$   
 $C(H)(COONa))_{112}-$ ; W is H.

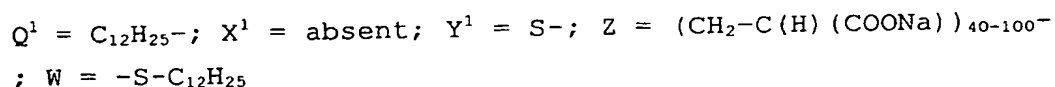
**Example 4 Synthesis of double-endcapped poly(sodium  
10 acrylate)s for deliberate bridging**

The double-endcapped ( $\alpha,\omega$ )-bis-dodecylthiapoly(acrylate)  
used as said agent for deliberate bridging of lamellar  
droplets can be prepared by polymerising acrylic acid in  
15 the presence of a radical initiator, and alkylsulfides as  
chain transfer agents. The degree of polymerisation (DP)  
of the resulting polymer can be predicted according to the  
Mayo equation:  $1/DP = 1/DP_0 + C_{tr}*[CTA]/[AA]$   
where  $DP_0$  is the degree of polymerisation in the absence of  
20 chain transfer agent,  $C_{tr}$  is the chain transfer constant  
( $C_{tr} = 2 \cdot 10^{-4}$  for didodecylsulfide),  $[CTA]$  is the molar  
concentration of the chain transfer agent, and  $[AA]$  is the  
molar concentration of acrylic acid.  $DP_0$  can easily exceed  
the value of 1000 for acrylic polymers, and so this term  
25 can be neglected here, where the desired degree of  
polymerisation is 40-100.

These considerations lead to the following proposed  
procedure. To obtain the abovementioned desired polymer  
30 having a degree of polymerisation between 40 and 100 (ca.  
4000 < MW < ca. 10000), acrylic acid is dissolved in liquid  
didodecyl sulfide at 60-80°C in 0.16-0.43% by weight,

respectively. AIBN (2,2'-Azobisisobutyronitrile) is added in 0.23% by weight with respect to acrylic acid to initiate the polymerisation. The mixture is heated at 60-80°C for three hours. When the reaction is complete, one equivalent of powdered sodium hydroxide is added, and the precipitated desired polymer is removed, e.g. by filtration. The liquid didodecylsulfide can be re-used in another polymerisation reaction.

10 The chemical structure of the polymer reads, according to formula I:



15

#### Example 5

Another way of preparing a sample with a significantly higher proportion of double-endcapped dodecyl poly(acrylate) as bridging agent for lamellar droplets is by radical polymerisation of acrylic acid in dioxan solvent using dodecanethiol as chain transfer agent and lauryl peroxide initiator. One method to make this polymer is as follows:

25

Acrylic acid (36 g, 0.5 mol), dodecanethiol (10.1g, 0.05 mol), dioxan (150 ml) were charged into a polymerisation reactor. After purging the reactor with nitrogen for 30 minutes, Lauryl peroxide (1.2 g) was added and the temperature was raised to 60°C. The polymerisation was carried out for 10 hours. The polymer solution was cooled to room temperature, and was neutralised with sodium

30



hydroxide solution (20 g NaOH). The solvent was removed using a rotary evaporator and can be re-used in another polymerisation reaction. The polymer was dissolved in water and precipitated into acetone. After purification by two more dissolution/precipitation procedures, the polymer was characterised and was ready for use in liquid detergent products.

The weight average molecular weight (Mw), obtained by GPC and converted to polyacrylate standards is 9,000-13,000. Hence, the chemical structure of the polymer reads, according to formula I:

$Q^1 = C_{11}H_{23}-$ ;  $X^1 = \text{absent}$ ;  $Y^1 = -COO-$ ;  $Z = -(CH_2-C(H)(COONa))_{90-135}-$

$$W = -S-C_{12}H_{25}$$

### Liquid Detergent examples

## Examples 6

[illegible]

Lamellar droplet deflocculation	good	good	good	good	good	good	good	good	good
Viscosity (mPa.s. at 21s-1)	30	70	90	100	70	230	60	100	1900

Deflocculating polymer (ref) = polymer A11 from EP-A-346,995

Deflocculating polymer (1) = polymer of Example 1 with a MW = 7800

Deflocculating polymer (2) = polymer of Example 5 with a MW = 9000 - 13000.

The results show that polymer (1) has similar deflocculating ability as the reference polymer. Differences are observed in effect on physical stability. Polymer (1) is somewhat more efficient in obtaining stability than the reference polymer. Furthermore, the results suggest that polymer (2) works as a bridging and viscosity enhancing polymer. The viscosity of example 6k is much higher than the reference systems 6f and 6c.

#### Examples 7

20 Component	%w/w		
	7a	7b	7c
LAS-acid	16.5	16.5	16.5
Nonionic (Dobanol 25-7)	9	9	9
Oleic acid (Priolene 6907)	4.5	4.5	4.5
Zeolite	15	15	15
KOH, neutralisation of acid and pH to 8.5			
Citric Acid	8.2	8.2	8.2
Glycerol	2.0	2.0	2.0

41

Borax	1.5	1.5	1.5
Deflocculating polymer (ref)	1.0		
Deflocculating polymer (1)		0.5	1.0
Protease	0.38	0.38	0.38
Termamyl	0.07	0.07	0.07
Lipolase	0.2	0.2	0.2
Oily soil release polymer	0.5	0.5	0.5
Aquaperle			
Further minors	0.9	0.9	0.9
Water			to 100%
Physical properties:			
Lamellar droplet	good	good	very
deflocculation			good
Physical stability	border-	OK	OK
	line		
Viscosity (mPa.s at 21s-1)	670	1250	1010

Deflocculating polymer (ref) = polymer A11 from EP 346,995  
 Deflocculating polymer (1) = polymer of Example 1 with a  
 MW = 7800

5

The results show that polymer (1) has better deflocculating ability as the reference polymer. The viscosities of the products are all in the range of good consumer acceptability for a pourable liquid.

10 The overall conclusion is that polymer (1) is more effective in obtaining the desired physical properties than the reference polymer.

#### Examples 8

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Component	%w/w		
	8a	8b	8c
LAS-acid	13.5	13.5	13.5
Nonionic (Dobanol 25-7)	4.5	4.5	4.5
Glycerol	4.37	4.37	4.37
Borax	2.79	2.79	2.79
STPP	18	18	18
KOH, neutralisation of acids to a pH of 7.5			
Deflocculating polymer (ref)	0.6		
Deflocculating polymer (1)		0.5	1.0
Protease	0.5	0.5	0.5
Lipolase	0.3	0.3	0.3
Oily soil release polymer	0.5	0.5	0.5
Aquaperle			
Antifoam	0.4	0.4	0.4
Perfume	0.4	0.4	0.4
Fluorescer	0.04	0.04	0.04
Water			to 100%
Physical properties:			
Lamellar droplet deflocculation	border- line	good	good
Physical stability	border- line	good	good
Viscosity (mP.a.s at 21s-1)	630	510	1380

Deflocculating polymer (ref) = polymer A11 from EP 346,995  
 5 Deflocculating polymer (1) = polymer of Example 1 with a  
 MW = 7800

The results show that polymer (1) has better deflocculating ability as the reference polymer. The overall conclusion is that polymer (1) is more efficient in obtaining the  
5 desired physical properties than the reference polymer.

In the light of this disclosure, modifications of the described examples, as well as other Examples, all within the scope of the present invention as defined by the  
10 appended claims, will now become apparent to persons skilled in the art.

## Claims

1. An oligomer or polymer of formula (I)



wherein  $Q^1$ -represents a hydrophobic moiety,  $-X^1$ - and  $-Y^1$ - are independently each absent or represent a suitable linking group,  $-Z$ - represents a hydrophilic chain; and  $-W$  represents hydrogen or a group of formula  $-Y^2-X^2-Q^2$ , each of  $-X^2$ ,  $-Y^2$  and  $-Q^2$  being independently selected from the values for  $X^1$ ,  $Y^1$  and  $Q^1$  as hereinbefore defined.

2. An oligomer or polymer according to claim 1, wherein  $Q^1$ - represents any optionally substituted  $C_5$ - $C_{30}$  alkyl,  $C_5$ - $C_{30}$  alkenyl or  $C_5$ - $C_{30}$  aralkyl group or else is a hydrophobic monomer residue, preferably, a hydrophobically modified TEMPO moiety.

3. An oligomer or polymer according to claim 1 or claim 2, wherein  $-X^1$ - is absent or represents a group of formula  $(-CH_2-)_n$  wherein  $n$  is 1 or 2 or  $X^1$  is phenyl.

4. An oligomer or polymer according to any preceding claim, wherein  $-Y^1$ - is absent or represents a carbonyl group, an ester linkage, a hydroxy  $C_{1-15}$  alkyl group or a silyl group of formula  $-SiR^1R^2$  where  $R^1$  and  $R^2$  independently represent  $-CH_3$  or  $-C_2H_5$ .

5. An oligomer or polymer according to any of claims 1-3, wherein  $-W$  is other than hydrogen and  $-Y^1$ - is selected from thia-, aza-, carboxy- (i.e. ester), carboxy aza-, phosphoryl-, phosphonyl- or phosphinyl- linkages.

6. An oligomer or polymer according to any preceding claim, wherein -Z- is selected from unsaturated acids and their corresponding salts, ethers, alcohols, aldehydes, ketones or esters, any of which have from 1 to 6 carbon atom; or -Z- is selected from cyclic monomer units which are unsaturated or comprise one or more groups capable of forming intermonomer linkage; or -Z- is selected from glycerol, polyalkylene oxide(s) and the unsaturated polyalcohol(s).
7. An oligomer or polymer according to any preceding claim, wherein -W represents hydrogen.
8. An oligomer or polymer according to any of claims 1-6, wherein -W represents a group of formula  $-Y^2 -X^2 -Q^2$  wherein respectively,  $X^2$ ,  $Y^2$  and  $Q^2$  are the same as  $X^1$ ,  $Y^1$  and  $Q^1$ .
9. An oligomer or polymer according to any preceding claim having a number average molecular weight of from 500 to 50,000.
10. A batch or sample of oligomer and/or polymer material comprising at least 50%, preferably at least 55%, more preferably at least 60%, still more preferably at least 65%, yet more preferably at least 70%, especially 75%, 80%, 85% or 95% by weight of an oligomer and/or polymer material according to any preceding claim.
11. A method of preparing an oligomer or polymer according to any preceding claim, the method comprising reacting a compound of formula (IV)



wherein  $Q^1$ ,  $X^1$  and  $Y^1$  are as hereinbefore defined and  $Y^2$  is a reactive hydrogen, or a free radical with a precursor material, in the presence of an initiator.

12. A method of preparing an oligomer or polymer according to any of claims 1-9, the method comprising reacting a compound of formula (V)



wherein  $Q^1$  is as hereinbefore defined with a precursor material as hereinbefore defined and  $Q^1-G-Q^1$  is a molecule capable of cleavage to form a radical of formula  $Q^1-X^1-Y^1$ .

13. A liquid detergent composition comprising a dispersion of lamellar droplets in an aqueous continuous phase, the composition further comprising an oligomer or polymer of formula (I), according to any of claims 1-9, or a sample or batch of oligomer or polymer material according to claim 10.

14. A composition according to claim 13, the composition comprising both at least one oligomer or polymer according to claim 7 and at least one oligomer or polymer according to any of claims 1-6, wherein -W represents a group of formula  $-Y^2-X^2-Q^2$  wherein  $X^2$ ,  $Y^2$  and  $Q^2$  are as defined in claim 1.

15. A composition according to claim 13 or claim 14, which composition comprises from 0.01 to 5% by weight in total of



the one or more oligomers or polymers according to any of claims 1 to 9 of a sample or batch of oligomer and/or polymer material according to claim 10.

# INTERNATIONAL SEARCH REPORT

national Application No  
PCT/EP 98/03005

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D3/37 C08F220/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 458 599 A (UNILEVER) 27 November 1991 ---	
A	EP 0 623 670 A (ALBRIGHT & WILSON LTD.) 9 November 1994 cited in the application ---	
A	US 5 489 397 A (P. BAINBRIDGE) 6 February 1996 cited in the application ---	
A	WO 96 02622 A (BASF CORP.) 1 February 1996 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 458599	A	27-11-1991	AU 636753 B	06-05-1993
			AU 7725891 A	28-11-1991
			CA 2042979 A	26-11-1991
			DE 69124420 D	13-03-1997
			DE 69124420 T	15-05-1997
			ES 2097793 T	16-04-1997
			JP 4228680 A	18-08-1992
			KR 9410047 B	21-10-1994
EP 623670	A	09-11-1994	AU 678572 B	05-06-1997
			AU 6197994 A	10-11-1994
			BG 98755 A	31-05-1995
			BR 9401051 A	06-12-1994
			CA 2123017 A	08-11-1994
			CN 1100339 A	22-03-1995
			CZ 9401130 A	15-03-1995
			FI 942106 A	08-11-1994
			GB 2279080 A, B	21-12-1994
			HU 68705 A	28-07-1995
			IL 109586 A	05-04-1998
			JP 7126696 A	16-05-1995
			NO 941720 A	08-11-1994
			NZ 260488 A	25-06-1996
			SK 53294 A	12-04-1995
			ZA 9403170 A	17-01-1995
			CN 1098739 A	15-02-1995
			CA 2138185 A	16-06-1995
			EP 0658620 A	21-06-1995
			GB 2288409 A, B	18-10-1995
			NO 944873 A	16-06-1995
US 5489397	A	06-02-1996	US 5599784 A	04-02-1997
WO 9602622	A	01-02-1996	US 5536440 A	16-07-1996
			US 5534183 A	09-07-1996
			AU 2981495 A	16-02-1996
			EP 0770122 A	02-05-1997
			JP 10502694 T	10-03-1998